

PATENT COOPERATION TREATY
PCT
INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY
(Chapter II of the Patent Cooperation Treaty)
(PCT Article 36 and Rule 70)

Applicant's or agent's file reference M/45198-PCT	FOR FURTHER ACTION		See Form PCT/PEA/416
International application No. PCT/EP2004/008397	International filing date (<i>day/month/year</i>) 27.07.2004	Priority date (<i>day/month/year</i>) 28.07.2003	
International Patent Classification (IPC) or national classification and IPC C25B11/04, C23C18/02, C01G19/04			
Applicant DE NORA ELETTRODI S.P.A. et al.			

1.	This report is the international preliminary examination report, established by this International Preliminary Examining Authority under Article 35 and transmitted to the applicant according to Article 36.
2.	This REPORT consists of a total of 5 sheets, including this cover sheet.
3.	This report is also accompanied by ANNEXES, comprising: <ul style="list-style-type: none"> a. <input checked="" type="checkbox"/> <i>sent to the applicant and to the International Bureau</i> a total of 3 sheets, as follows: <ul style="list-style-type: none"> <input type="checkbox"/> sheets of the description, claims and/or drawings which have been amended and are the basis of this report and/or sheets containing rectifications authorized by this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions). <input type="checkbox"/> sheets which supersede earlier sheets, but which this Authority considers contain an amendment that goes beyond the disclosure in the international application as filed, as indicated in item 4 of Box No. I and the Supplemental Box. b. <input type="checkbox"/> (<i>sent to the International Bureau only</i>) a total of (indicate type and number of electronic carrier(s)) , containing a sequence listing and/or tables related thereto, in computer readable form only, as indicated in the Supplemental Box Relating to Sequence Listing (see Section 802 of the Administrative Instructions).

4.	This report contains indications relating to the following items: <ul style="list-style-type: none"> <input checked="" type="checkbox"/> Box No. I Basis of the opinion <input type="checkbox"/> Box No. II Priority <input type="checkbox"/> Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability <input type="checkbox"/> Box No. IV Lack of unity of invention <input checked="" type="checkbox"/> Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement <input type="checkbox"/> Box No. VI Certain documents cited <input type="checkbox"/> Box No. VII Certain defects in the international application <input type="checkbox"/> Box No. VIII Certain observations on the international application
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Date of submission of the demand 27.05.2005	Date of completion of this report 20.10.2005
Name and mailing address of the international preliminary examining authority: <div style="display: flex; align-items: center;"> <div> European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465 </div> </div>	Authorized Officer Teppo, K-M Telephone No. +49 89 2399-8130



**INTERNATIONAL PRELIMINARY REPORT
ON PATENTABILITY**

Box No. I Basis of the report

1. With regard to the **language**, this report is based on the international application in the language in which it was filed, unless otherwise indicated under this item.
- ☐ This report is based on translations from the original language into the following language, which is the language of a translation furnished for the purposes of:
- ☐ international search (under Rules 12.3 and 23.1(b))
 - ☐ publication of the international application (under Rule 12.4)
 - ☐ international preliminary examination (under Rules 55.2 and/or 55.3)
2. With regard to the **elements*** of the international application, this report is based on *(replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report)*:

Description, Pages

1-9 as originally filed

Claims, Numbers

1-22 received on 10.10.2005 with letter of 10.10.2005

- ☐ a sequence listing and/or any related table(s) - see Supplemental Box Relating to Sequence Listing
3. ☐ The amendments have resulted in the cancellation of:
- ☐ the description, pages
 - ☐ the claims, Nos.
 - ☐ the drawings, sheets/figs
 - ☐ the sequence listing (*specify*):
 - ☐ any table(s) related to sequence listing (*specify*):
4. ☐ This report has been established as if (some of) the amendments annexed to this report and listed below had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).
- ☐ the description, pages
 - ☐ the claims, Nos.
 - ☐ the drawings, sheets/figs
 - ☐ the sequence listing (*specify*):
 - ☐ any table(s) related to sequence listing (*specify*):

* If item 4 applies, some or all of these sheets may be marked "superseded."

**INTERNATIONAL PRELIMINARY REPORT
ON PATENTABILITY**

International application No.
PCT/EP2004/008397

Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes: Claims	1-22
	No: Claims	
Inventive step (IS)	Yes: Claims	1-22
	No: Claims	
Industrial applicability (IA)	Yes: Claims	1-22
	No: Claims	

2. Citations and explanations (Rule 70.7):

see separate sheet

INTERNATIONAL PRELIMINARY
REPORT ON PATENTABILITY
(SEPARATE SHEET)

PCT/EP2004/008397

Re Item V.

1. The following documents are referred to in this communication:
D1: SU 541 849 A (DOBROKHOTOVA T F) 5 January 1977 (1977-01-05)
D2: EP-A-0 479 423 (ICI PLC) 8 April 1992 (1992-04-08)
D3: US-A-5 868 913 (HODGSON DAVID RONALD) 9 February 1999 (1999-02-09)
D4: US-A-4 941 953 (MATSUMOTO YUKIEI ET AL) 17 July 1990 (1990-07-17)
D5: US-A-5 314 534 (GIERSBERG JOACHIM ET AL) 24 May 1994 (1994-05-24)
D6: US-A-4 873 352 (KOBASHI TOSHIYUKI ET AL) 10 October 1989 (1989-10-10)
D7: EP-A-0 302 738 (JAPAN EXLAN CO LTD) 8 February 1989 (1989-02-08)
D8: GB-A-1 373 712
2. Document D8 was introduced into the proceedings by the examiner. A copy of D8 was sent to the applicant with the first opinion.
3. D1 was translated due to the applicant's allegation that this document had been incorrectly translated in the abstract available. This allegation is now fully accepted that the translation of D1 is available. Translation of D1 is enclosed to this report. All objections in respect of D1 are hereby cancelled.
4. Document D8, which is regarded as the closest prior art document, discloses a method for the manufacturing of an electrode, comprising the application of a precursor for the pyrolytic formation of a tin-containing coating to a substrate of a valve metal, followed by the execution of thermal treatment, wherein the precursor solution comprises stannic hydroxychloride (see D8, the examples 1 and 6). The presence of both stannous chloride dihydrate and hydrogen peroxide in the solution to be applied to the titanium electrode (e.g. anode) gives necessarily a reaction where the "precursor" solution comprises stannic hydroxychloride, at least in small percentages.
The subject-matters of claims 1, 11, 14 and 20 differ from this in that the stannic hydroxychloride precursor claimed is non-stoichiometric. The stannic hydroxychloride disclosed in D8 must be assumed to stoichiometric, since nothing is mentioned on it being non-stoichiometric. I.e. there is also no method of decreasing the Cl:Sn ratio in the precursor solution disclosed in D8.

The problem to be solved can thus be formulated as how to provide an improved precursor solution for providing tin-containing coatings on electrodes.

Document D5 is not related to coating anodes but it discloses coating glasses with a precursor solution comprising both a stoichiometric stannic hydroxychloride and a non-stoichiometric stannic hydroxyoxalate (the ratio of Sn:Cl should be 1:1; in D5, see the claims 1 and 3). However, there is no hint in D5 to vary the stoichiometry of the stannic hydroxychloride.

5. Document D2 discloses an electrode (e.g. anode) provided with an electrocatalytic coating comprising tin in form of mixed oxide.
6. Thus, none of the available prior art documents discloses a non-stoichiometric stannic hydroxychloride precursor compound nor a method for its manufacture. With the use of such a non-stoichiometric solution for manufacturing of SnO_2 coatings, coatings with improved stability and electrocatalytic performance are manufactured.
Therefore, the subject-matters of claims 1, 11, 14 and 20 meet the requirements of Art. 33(1) and 33(3) PCT.
7. The related dependent claims 2-10, 12, 13, 15-19, 21 and 22 also meet the requirements of the PCT with respect to novelty and inventive step.

CLAIMS:

1. A method for the manufacturing of an electrode, comprising the application of a solution of a precursor for the pyrolytic formation of a tin-containing coating to a substrate of a valve metal, followed by the execution of thermal treatment, wherein the precursor solution comprises a stannic hydroxychloride species selected from a non-stoichiometric compound expressed by the formula $\text{Sn}(\text{OH})_{2+x}\text{Cl}_{2-x}\cdot n\text{H}_2\text{O}$, and a compound expressed by the formula $\text{SnO}(\text{H}_2\text{O})_n\text{R}_{2-x}\text{Cl}_x$, wherein R is an organic substituent.
2. The method of claim 1 wherein the Cl:Sn molar ratio is comprised between 1 and 1.9.
3. The method of claim 1 or 2 wherein R is the acetic group ($\text{CH}_3\text{COO}-$).
4. The method of any one of the previous claims further comprising a precursor of at least one noble metal.
5. The method of claim 4 wherein said precursor of at least one noble metal is a chlorinated precursor of iridium or ruthenium.
6. The method of claim 5 wherein said chlorinated precursor of iridium is H_2IrCl_6 .
7. The method of anyone of claims 1 to 6 wherein a valve metal is titanium or titanium alloy optionally provided with a ceramic pre-layer.
8. The method of claim 7 wherein the ceramic pre-layer comprises titanium dioxide.
9. The method of anyone of claims 1 to 8 wherein said application of the solution is effected in multiple coats, each followed by a thermal treatment.

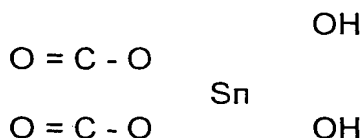
10. The method of anyone of claims 1 to 9 wherein said thermal treatment is a pyrolysis at a temperature comprised between 350 and 800°C, optionally preceded by a drying at a temperature comprised between 80 and 200°C.
11. An anode provided with an electrocatalytic coating comprising tin, preferably tetravalent and in form of mixed oxide, prepared by the method of any one of the previous claims.
12. The anode of claim 11, prepared by the method of claim 4, wherein said coating has electrocatalytic properties toward the chlorine evolution reaction and said at least one noble metal is ruthenium.
13. The anode of claim 12, prepared by the method of claim 4, wherein said coating has electrocatalytic properties toward the oxygen evolution reaction and said at least one noble metal is iridium.
14. A solution of a precursor for the pyrolytic formation of a tin-containing coating, comprising a stannic hydroxychloride species selected from a non-stoichiometric compound expressed by the formula $\text{Sn}(\text{OH})_{2+x}\text{Cl}_{2-x} \cdot n\text{H}_2\text{O}$ and a compound expressed by the formula $\text{SnO}(\text{H}_2\text{O})_n \text{R}_{2-x}\text{Cl}_x$, wherein R is an organic substituent.
15. The solution of claim 14 wherein the Cl:Sn molar ratio is comprised between 1 and 1.9.
16. The solution of claim 14 or 15 wherein R is the acetic group.
17. The solution of any one of claim 14 to 16 further comprising a precursor of at least one noble metal.
18. The solution of claim 17 wherein said precursor of at least one noble metal is a chlorinated pre-cursor of iridium or ruthenium.
19. The solution of claim 18 wherein said chlorinated precursor of iridium is

H_2IrCl_6 .

20. A method for the manufacturing of a precursor solution for the pyrolytic formation of a tin-containing coating comprising the addition of hydrogen peroxide to a stannous chloride solution, optionally under temperature and redox potential control., wherein the Cl:Sn ratio in the solution is decreased by subsequent reduction of metallic tin and further addition of hydrogen peroxide, optionally under temperature and redox potential control.
21. The method of claim 20 wherein said stannous chloride solution further contains a precursor of an organic substituent.
22. The method of claim 21 wherein said precursor of an organic substituent is acetic acid.

(54) OXALOSTANNIC ACID AS AN INTERMEDIATE IN THE PRODUCTION OF STANNIC DIOXIDE, AND A METHOD FOR PRODUCING IT

The invention relates to oxalostannic acid of the formula



used as an intermediate in the production of stannic dioxide, and a method for producing it.

Stannic dioxide is used in the manufacture of transparent, conducting, semiconductive layers, heat-resistant, high-resistance, direct-current and alternating resistors of various types, catalysers, enamels, ion-exchange materials and means for preventing ice-formation and condensation on the windows of motor vehicles, aircraft, ships and various appliances.

It is known that conducting, semiconductive layers of stannic dioxide are produced by treating glass heated to 500 - 550°C with solutions of stannic chloride SnCl_4 .

However, the use of stannic chloride is accompanied by the release of a large quantity of hydrochloric acid (into waste water and the atmosphere), which causes substantial corrosion of equipment.

The proposed compound - oxalostannic acid - is produced by oxidising freshly prepared stannous oxalate with hydrogen peroxide in an aqueous medium at 20 - 100°C.

Stannous oxalate oxidises completely when oxidised with hydrogen peroxide, forming a transparent solution of oxalostannic acid.

Example 1. 500 g of freshly prepared stannous oxalate is added to 2 l of water, 300 ml of a solution of 30% hydrogen peroxide is added with stirring, stirring is carried out at 70 - 80°C, and the resulting transparent solution of oxalostannic acid with a pH of 1.65 contains 156.5 g/l of stannic dioxide. The solution can be used to produce transparent semiconductive layers or powdered stannic dioxide.

Example 2. 2 l of water, 1 kg of freshly prepared stannous oxalate and 600 ml of 30% hydrogen peroxide are stirred, during which self-heating takes place, and the resulting transparent solution with a pH of 1.62 contains 279 g/l of stannic dioxide.

The potentiometric titration curve of a 0.2 M solution of oxalostannic acid with caustic soda has two points of equivalence, which testifies to the dibasic nature of the resulting acid.

The UV absorption spectra taken with a Perkin Elmer double-beam spectrophotometer in the 180 - 360 nm region for $1 \cdot 10^{-3}$ M solutions of $\text{Na}_2[\text{Sn}(\text{OH})_6]$, oxalostannic acid and oxalic acid show that oxalostannic acid is an individual chemical compound. The anion $[\text{Sn}(\text{OH})_4\text{C}_2\text{O}_4]^{2-}$ is present in the solution.

After dehydration (evaporation) or drying of the transparent solution, solid, air-dry oxalostannic acid is obtained in the form of a white powder with a bulk weight of 1.92 g/cm^3 , a density of 3.0 g/cm^3 and a solubility in water of 1.020 g/l at 25°C , the pH of the saturated solution being 1.60.

The air-dry acid contains (% by weight): 63.20 (63.50) stannic dioxide, 34.10 (34.50) oxalic acid and 2.70 (2.00) water, which corresponds to a molar ratio of 1 : 1 : 0.25. The stannic dioxide content is determined on the basis of weight, the oxalic acid content permanganometrically and the quantity of water either thermogravimetrically or by IR spectroscopy.

The air-dry preparation is x-ray amorphous, but an electron-diffraction pattern taken with an EG-100M electron-diffraction camera shows that the compound has a crystalline structure (see table).

Line no.	Line intensity I/I_1	Interplanar distance d
1	5.0	3.89
2	1.0	2.85
3	2.0	2.49
4	1.0	2.41
5	2.0	2.31
6	2.0	2.21
7	2.0	1.94
8	2.0	1.78
9	2.0	1.76
10	1.0	1.69
11	1.0	1.55
12	1.0	1.51
13	1.0	1.46
14	1.0	1.30
15	1.5	1.27
16	1.5	1.21
17	1.0	1.16
18	1.0	1.13
19	1.0	1.06
20	1.0	0.91
21	1.0	0.84
22	1.0	0.80

- A comparison of the interplanar distances and the intensity of the lines of oxalostannic acid, oxalic acid and known tetravalent tin compounds allows the conclusion that oxalostannic acid is a new individual compound with its own crystalline structure.

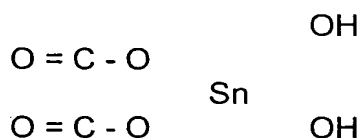
Thermogravimetric analysis of the preparation shows the presence of three effects with extreme temperatures of 170, 220 and 360°C. The last exothermal effect is not accompanied by loss of mass, and, according to data obtained from x-ray phase analysis, corresponds to the crystallisation of stannic dioxide SnO_2 (cassiterite) with the parameters $a = 4.73 \text{ \AA}$ and $c = 3.18 \text{ \AA}$.

- Data for IR absorption spectra (KBr tablets) for preparations fired at 170 and 220°C show that the first endothermal effect at 170°C corresponds to the removal of water, and the second at 220°C to the breakdown of the oxalate group.

Powders of resistive compositions based on stannic dioxide produced from oxalostannic acid, with antimony added after firing, are solid solutions based on stannic dioxide and have a low resistance.

Claims

1. Oxalostannic acid of the formula



as an intermediate in the production of stannic dioxide.

2. Method for producing the compound according to claim 1, characterised in that freshly prepared stannous oxalate is oxidised with hydrogen peroxide in an aqueous medium at 20 - 100°C.

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